# Coal-Ash Corrosion of Structural Alloys in Simulated Oxy-Fuel Environments

*K. Natesan and Z. Zeng*
*Argonne National Laboratory*

*25th Annual Conference on Fossil Energy Materials, Portland, OR, April 26-28, 2011*

*Work supported by DOE/Office of Fossil Energy, Advanced Research Materials Program*

# Outline

- *Background*
- *Objectives*
- *Materials and experimental procedure*
- *Alloys for evaluation*
- *Role of gas and ash environments*
- *Corrosion performance of alloys*
- *Project Summary*

# What and Why Oxy-Fuel Combustion

- *Global climate change - One of the causes identified is $CO_2$ increase in atmosphere - one of the source for $CO_2$ is exhaust from fossil fuel combustion plants*
- *Energy production (in particular, electricity) is expected to increase due to population increase and per capita increase in energy consumption*
- *To meet the energy needs fossil fuels (coal, gas, oil, etc.) will play a major part in production even with a projected increase from alternate sources*
- *To minimize $CO_2$ emission - current systems emphasize capture from power plants and sequestration*
- *Oxy-fuel combustion systems - recycle $CO_2$ to the boiler and/or compressor, use novel gas turbines, and emphasize reuse*

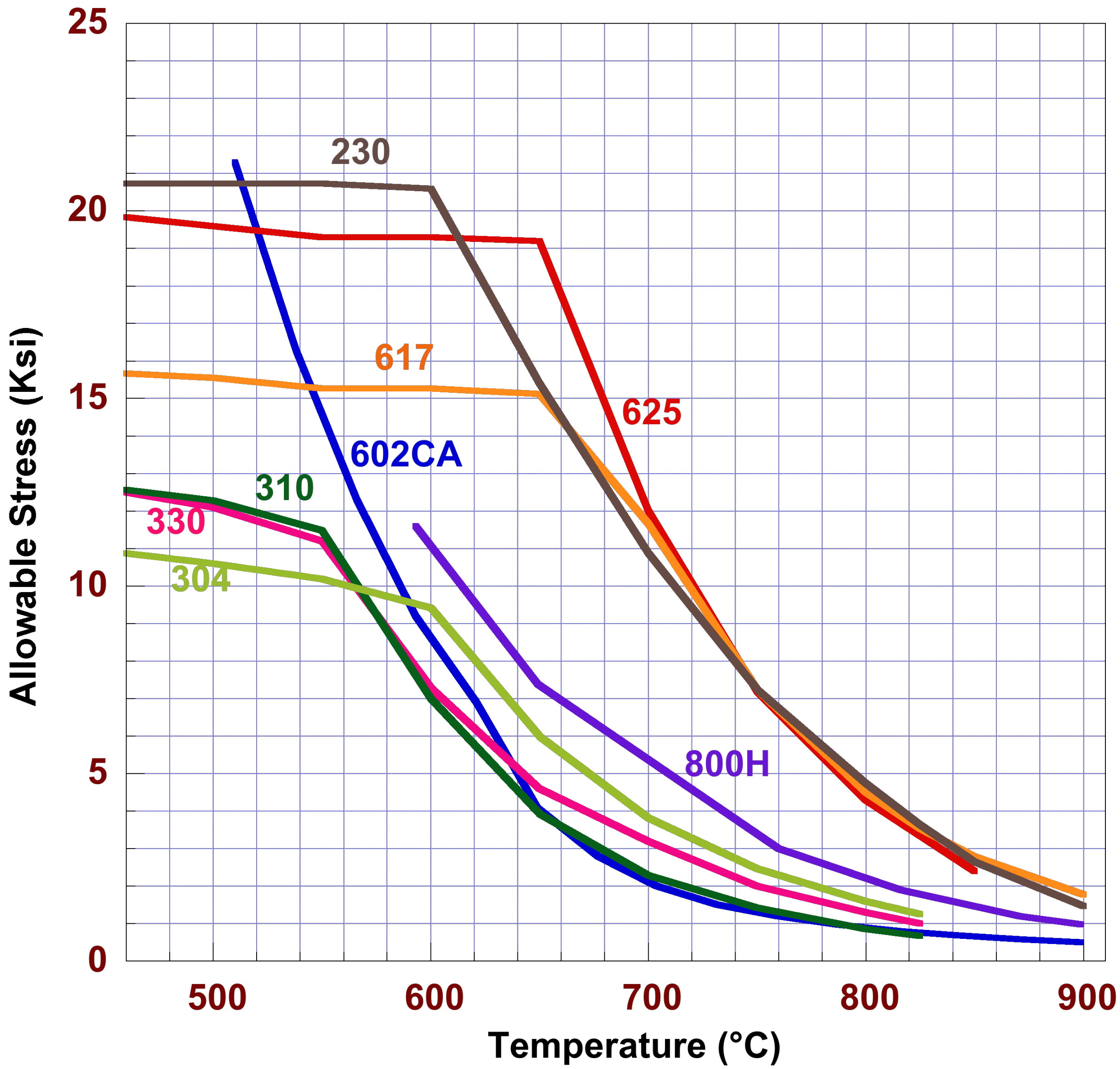
# *ANL Program Objectives*

- Evaluate oxidation/corrosion performance of metallic structural alloys in pure $CO_2$ and in $CO_2$-steam environments over a wide temperature range
- Establish the kinetics of scaling and internal penetration, if any, and develop correlations for long term performance
- Evaluate the effect of coal ash with trace concentrations of alkali, sulfur, and chlorine compounds on the corrosion performance
- Identify viable alloys for structural and gas turbine applications
- Develop alternate corrosion-resistant alloys and coatings
- Evaluate the influence of exposure environment on the mechanical properties (especially creep, fatigue, and creep-fatigue) of the candidate alloys

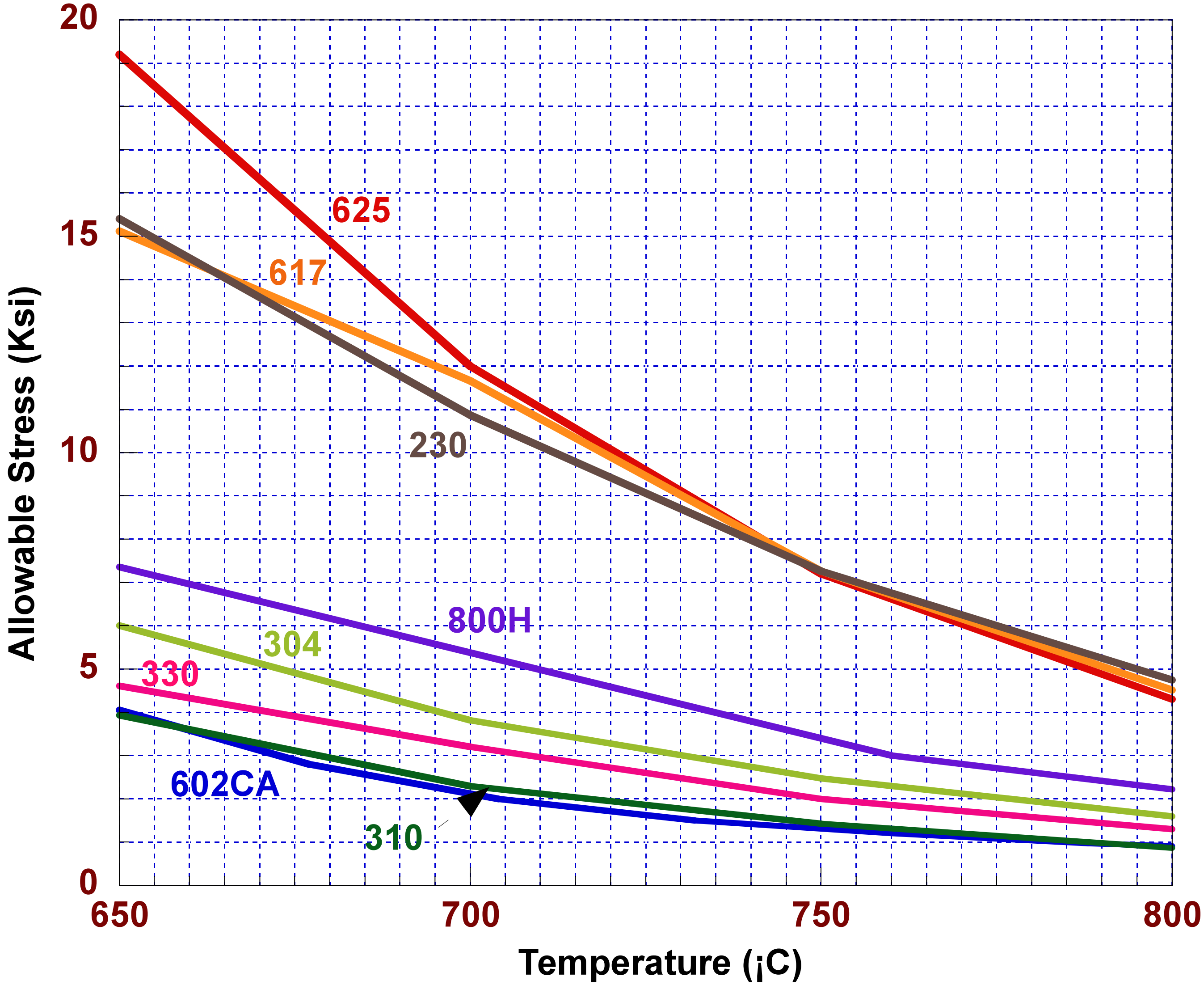
# Current List of Alloys in the Study

| Material | C | Cr | Ni | Mn | Si | Mo | Fe | Other |
|---|---|---|---|---|---|---|---|---|
| 153MA | 0.05 | 18.4 | 9.5 | 0.6 | 1.4 | 0.2 | Bal | N 0.05, Nb 0.07, V 0.2 |
| 800H | 0.08 | 20.1 | 31.7 | 1.0 | 0.2 | 0.3 | Bal | Al 0.4, Ti 0.3 |
| 330 | 0.05 | 10.0 | 35.0 | 1.5 | 1.25 | - | Bal | - |
| 333 | 0.05 | 25.0 | 45.0 | - | 1.0 | 3.0 | 18.0 | Co 3.0, W 3.0 |
| 617 | 0.08 | 21.6 | 53.6 | 0.1 | 0.1 | 9.5 | 0.9 | Co 12.5, Al 1.2, Ti 0.3 |
| 625 | 0.05 | 21.5 | Bal | 0.3 | 0.3 | 9.0 | 2.5 | Nb 3.7, Al 0.2, Ti 0.2 |
| 602CA | 0.19 | 25.1 | 62.6 | 0.1 | 0.1 | - | 9.3 | Al 2.3, Ti 0.13, Zr 0.19, Y 0.09 |
| 230 | 0.11 | 21.7 | 60.4 | 0.5 | 0.4 | 1.4 | 1.2 | W 14, Al 0.3, La 0.015 |
| 693 | 0.02 | 28.8 | Bal | 0.2 | 0.04 | 0.13 | 5.8 | Al 3.3, Nb 0.67, Ti 0.4, Zr 0.03 |
| 740 | 0.07 | 25.0 | Bal | 0.3 | 0.5 | 0.5 | 1.0 | Co 20.0, Ti 2.0, Al 0.8, Nb+Ta 2.0 |
| 718 | - | 19.0 | 52.0 | - | - | 3.0 | 19.0 | Nb 5.0, Al 0.5, Ti 0.9, B 0.002 |
| MA956 | - | 20.0 | - | - | - | - | Bal | Al 4.5, Ti 0.5, $Y_2O_3$ 0.6 |
| WASP | 0.07 | 20.0 | Bal | 0.1 | 0.1 | 5 | - | Al 1.4, Ti 3, Co 13.5 |
| Alloy 1 | | | Ni base alloy | | | | | |
| Alloy 2 | | | Ni base alloy | | | | | |

# ASME Code Allowable Stress Values



# ASME Code Allowable Stress Values at 650-800°C



## *Laboratory Test Details*

**Key variables: Temperature, time, alloy composition**

**Materials: Fe- and Ni-base alloys, coatings**

**Environment: $CO_2$, $CO_2$-steam, oxy-fuel gases with and without steam**

**Deposits: Simulated coal ash, alkali sulfates, alkali chloride**

**Ash mixture: 90% ($SiO_2$ :$Al_2O_3$:$Fe_2O_3$ = 1:1:1) and 10% ($Na_2SO_4$:$K_2SO_4$ = 1:1)**

**Test temperature range: 650-1000°C**

**Test times: up to 10,000 h**

**Specimen evaluation: weight change**
**scanning electron microscopy**
**energy dispersive X-ray analysis**
**X-ray diffraction**
**synchrotron nanobeam analysis**

## *Gas Chemistry Used in Experiments*

**Pure $CO_2$**

**$CO_2$ - 50% Steam**

**$CO_2$ - 3.97% Oxygen**

**$CO_2$ – 27.4% $H_2O$ - 3.97% $O_2$**

***Oxy-Fuel gas (high $pO_2$): 46.8% $CO_2$ - 25.4% $H_2O$ - 26.8% $O_2$ - 0.99% $SO_2$**

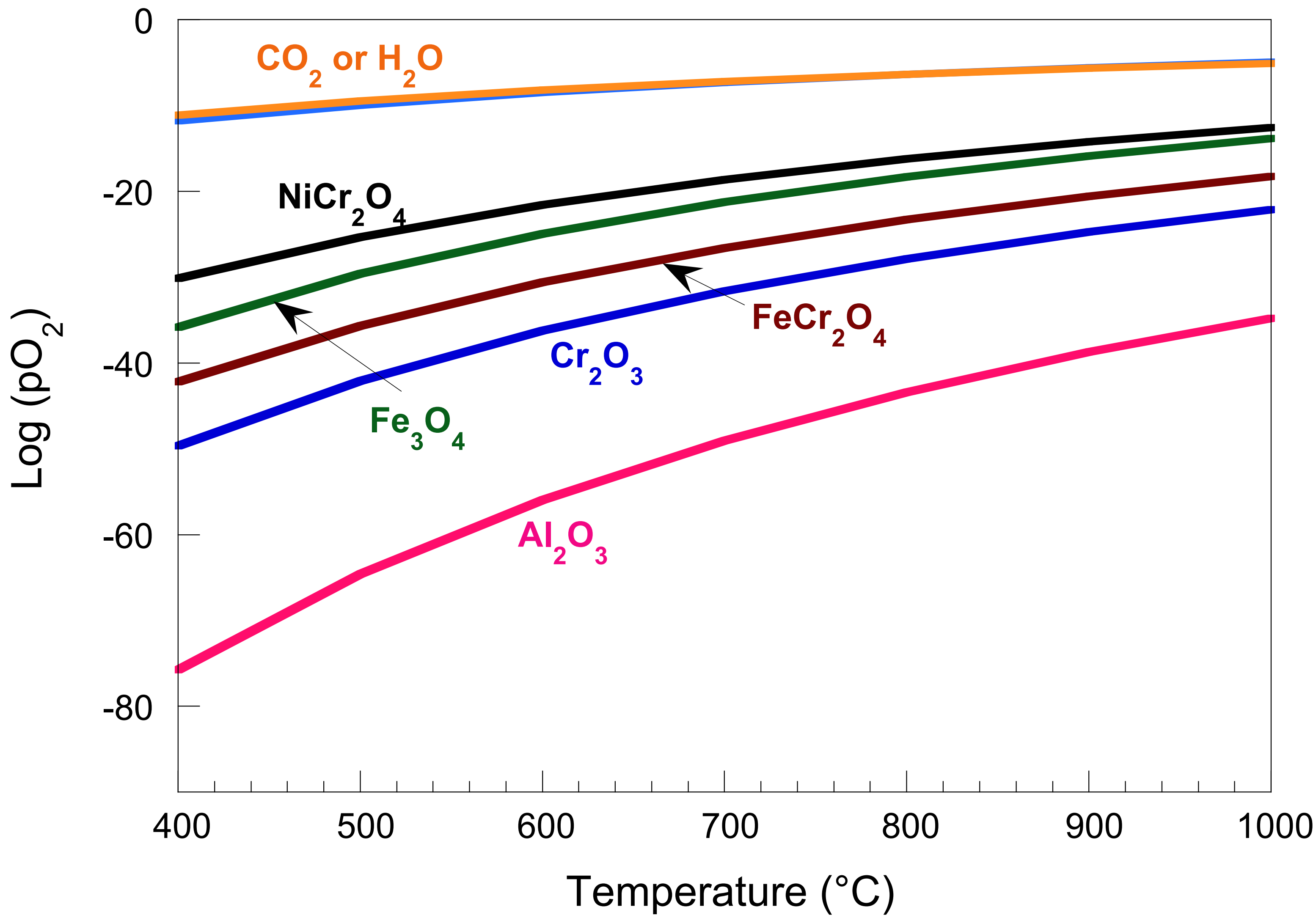
***High $pO_2$ gas without steam: 72.2% $CO_2$ - 26.8% $O_2$ - 0.99% $SO_2$**

***Oxy-Fuel gas (low $pO_2$): 68.14% $CO_2$ – 26.9% $H_2O$ - 3.97% $O_2$ - 0.99% $SO_2$**

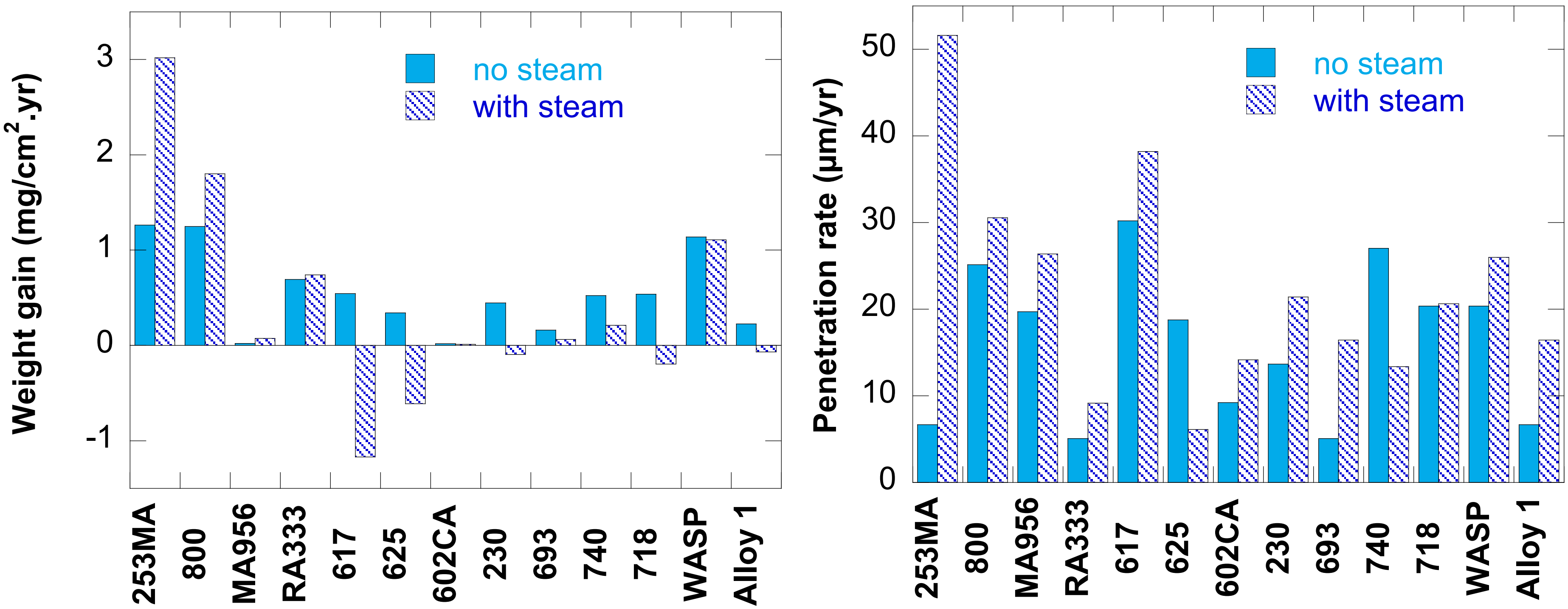
***Low $pO_2$ gas without steam: 95.04% $CO_2$ - 3.97% $O_2$ - 0.99% $SO_2$**

*** Indicates environments used in tests conducted in the presence of simulated ash and alkali sulfates**

# *Thermodynamic Stability of Oxide Phases in the Scale*



## *Alloy Penetration Rates in $CO_2$ - $H_2O$ - $O_2$ at 750ºC (no ash)*

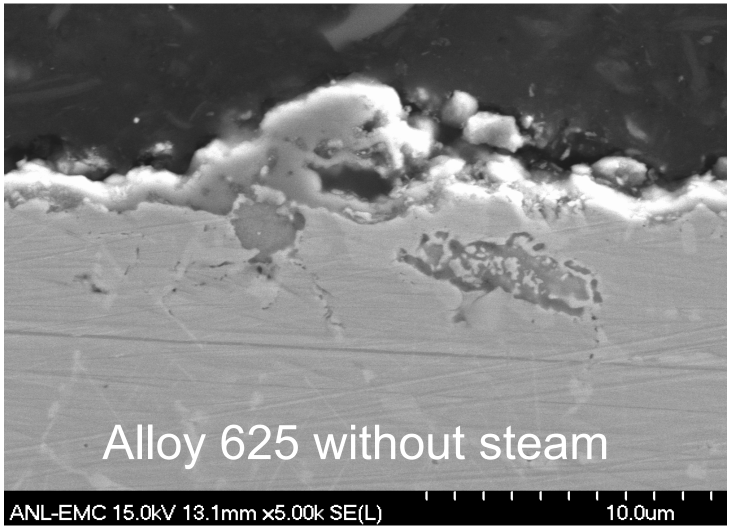


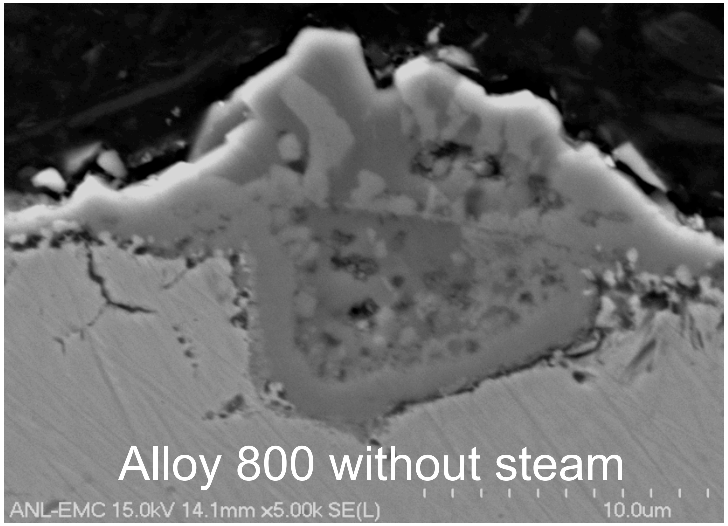

**No steam: $CO_2$ - 3.97% $O_2$**

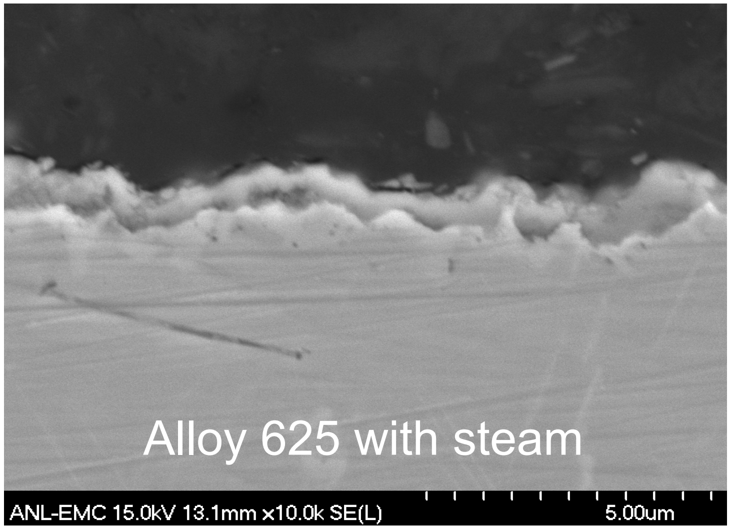
**With steam: $CO_2$ – 27.4% $H_2O$ - 3.97% $O_2$**

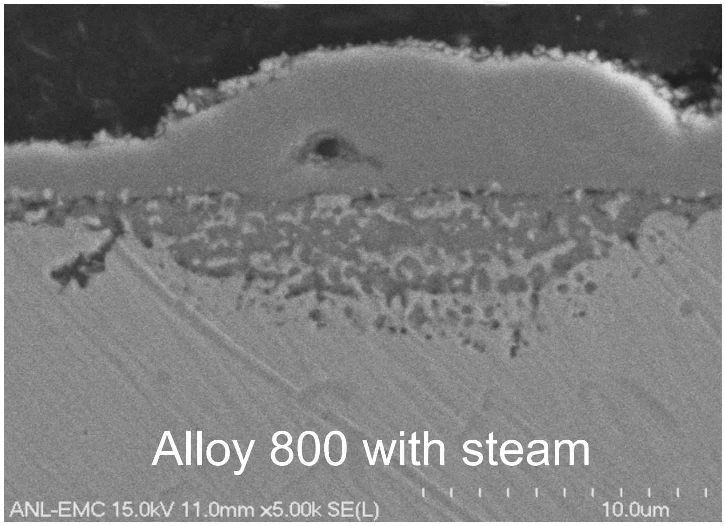
**High Cr, Al beneficial; Nb detrimental**

# Ni-base alloys performed better than Fe-base alloys

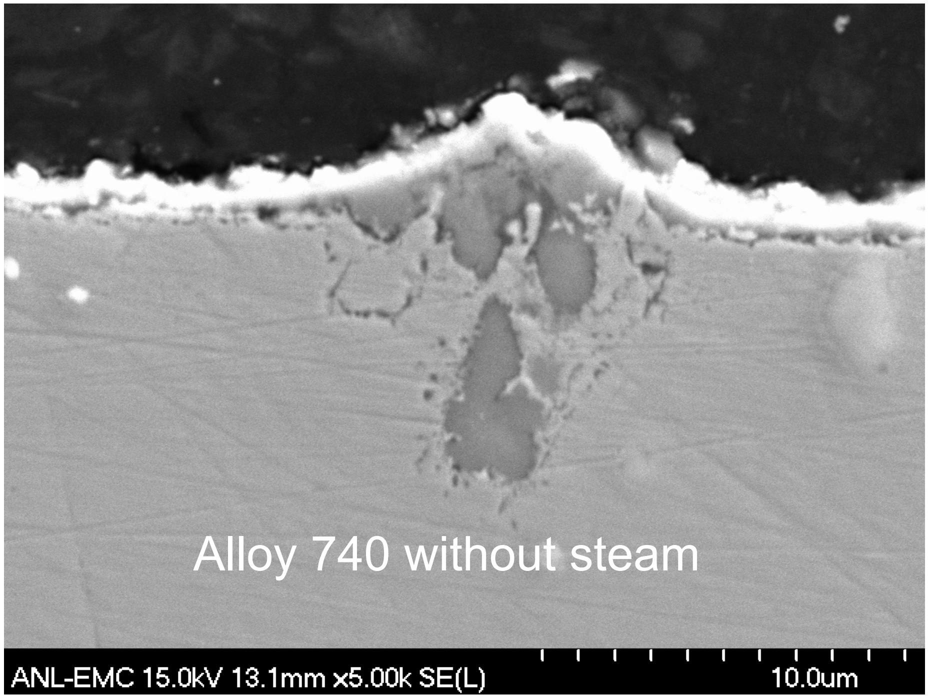


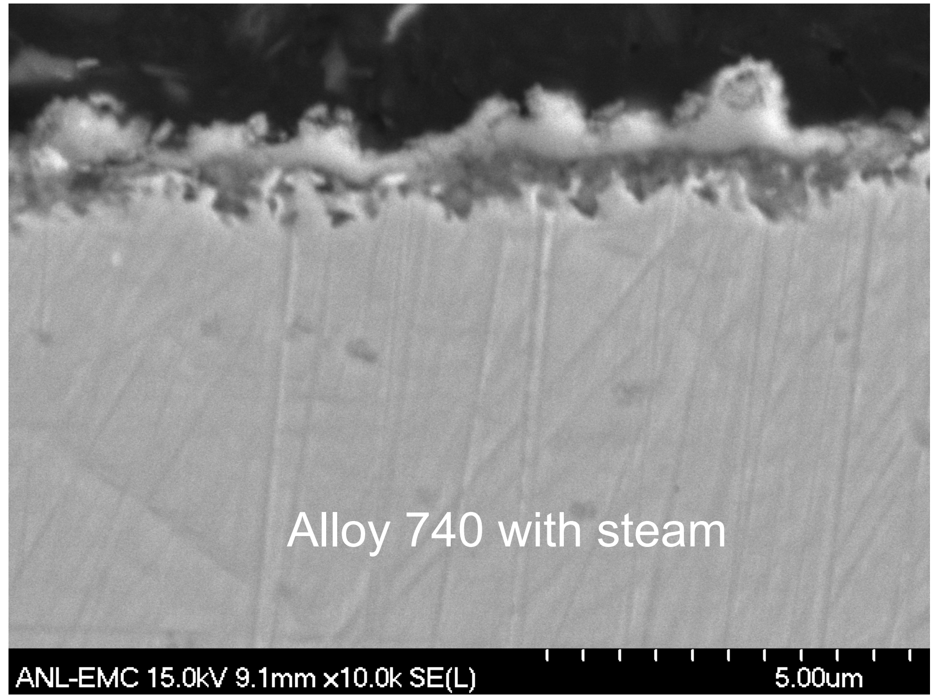



# *Ni-base Performance of Alloy 740 at 750°C*



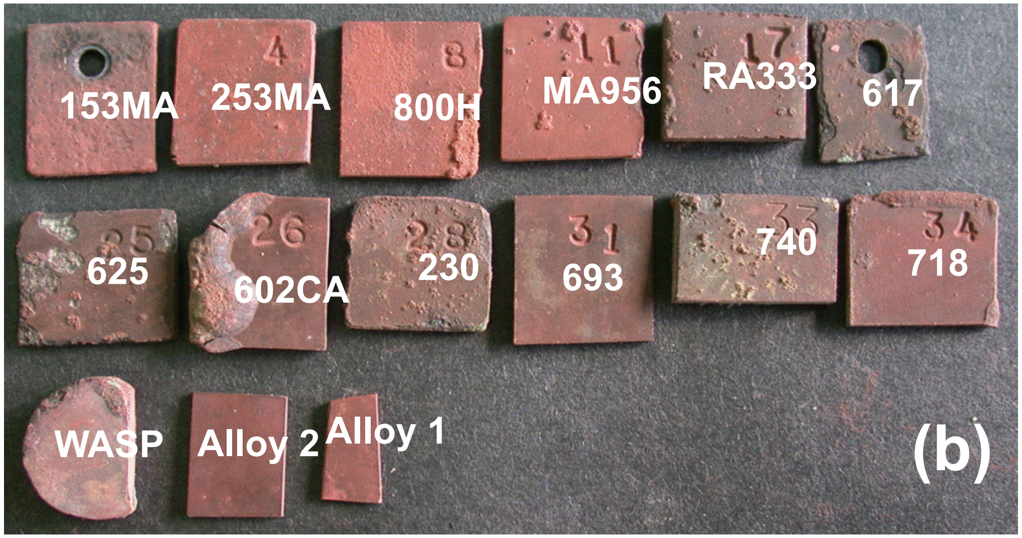

**No steam:** **$CO_2$ - 3.97% $O_2$**

**With steam:** **$CO_2$ – 27.4% $H_2O$ - 3.97% $O_2$**

# *Specimens after 1200-hr Exposure at 750°C to Ash and Low-$pO_2$*


with steam

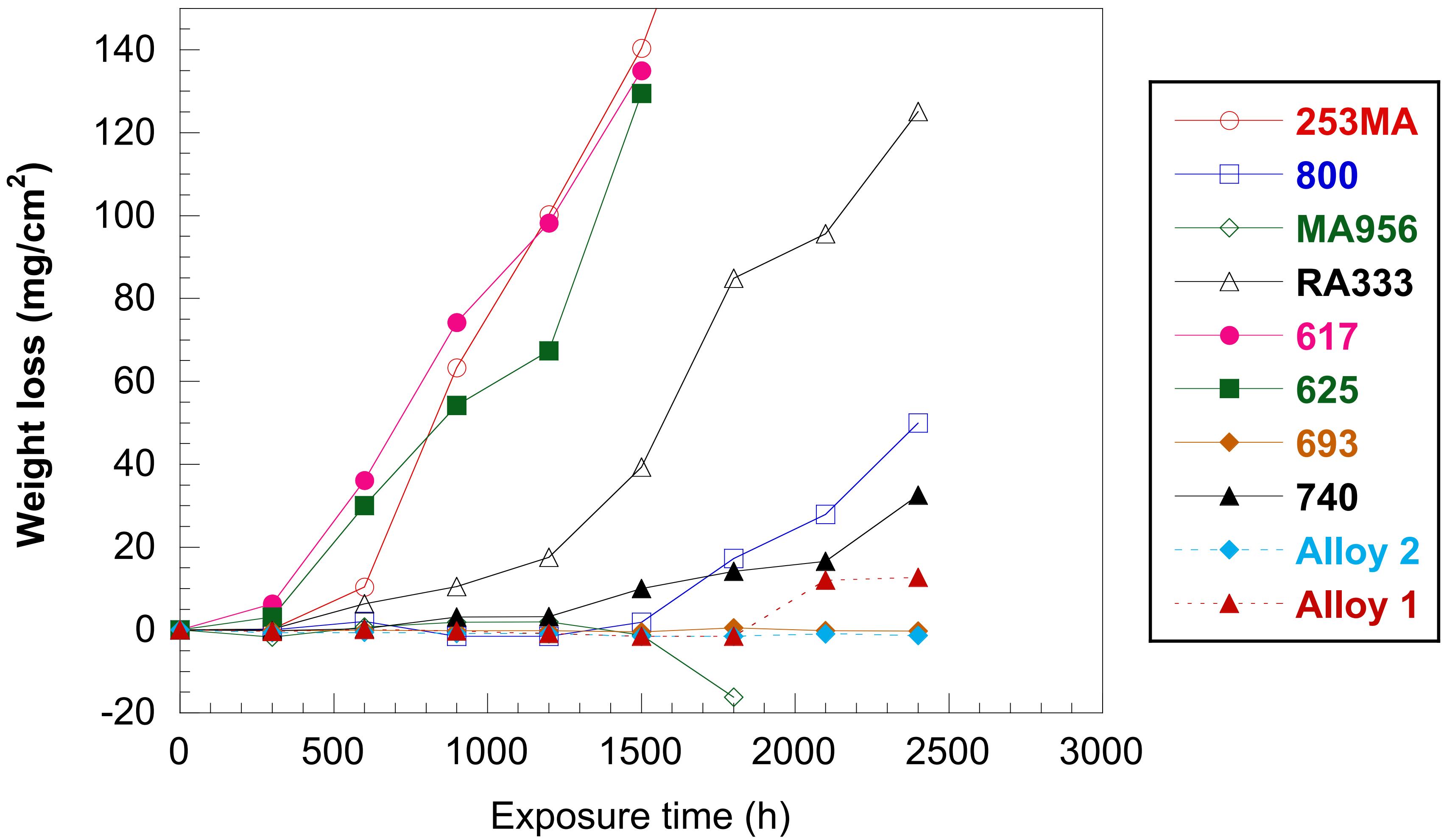
Uniform corrosion: 153MA, 253MA, 617
Localized corrosion: 800H, MA956, RA333, 625, 602CA, 230, 718, WASP, Alloy 1
No corrosion:  693, 740, Alloy 2



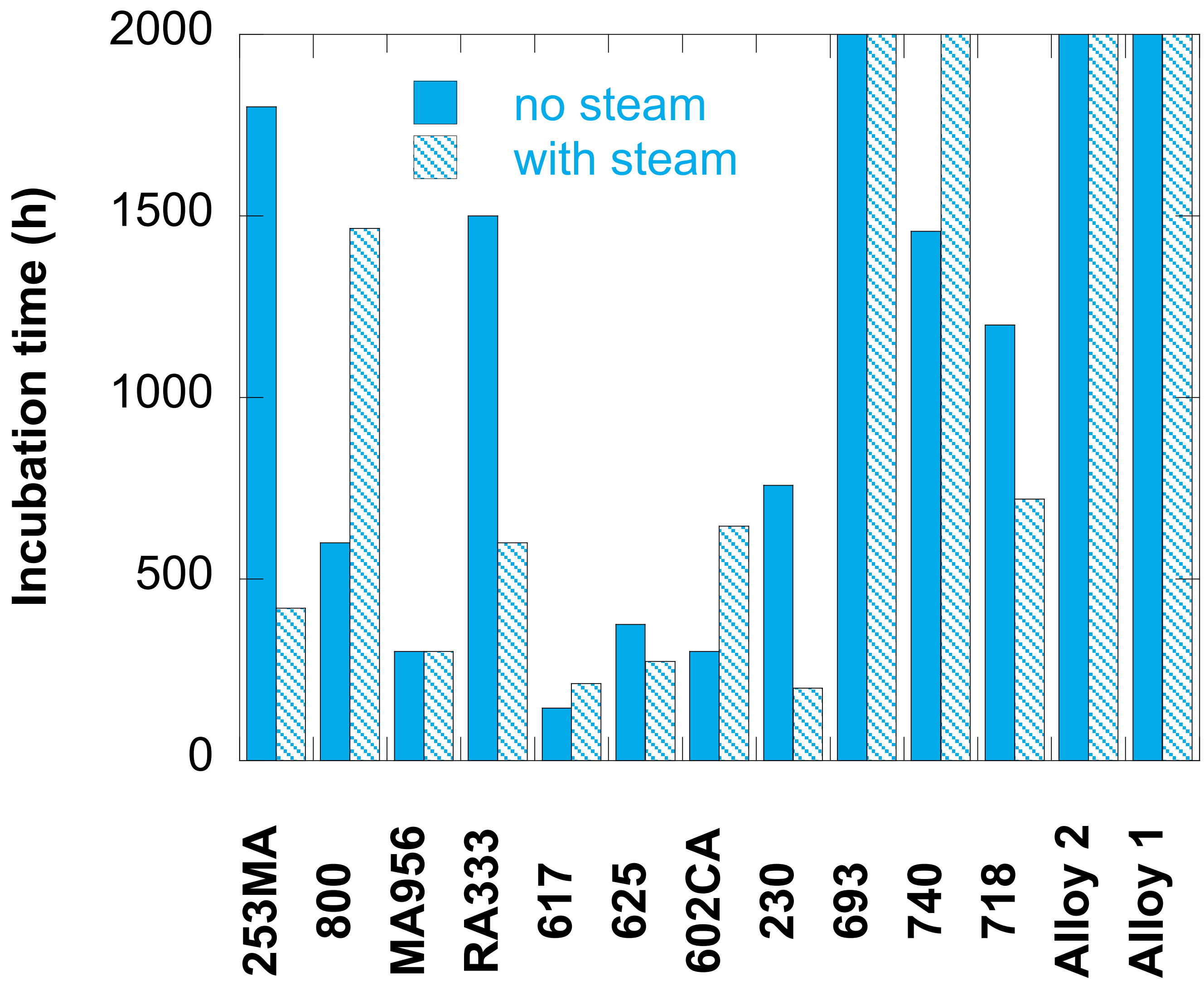

without steam

Uniform corrosion: 153MA
Localized corrosion: 800H, MA956, RA333, 617, 625, 602CA, 230, 718, WASP, 740
No corrosion: 253MA, 693, Alloys 1& 2

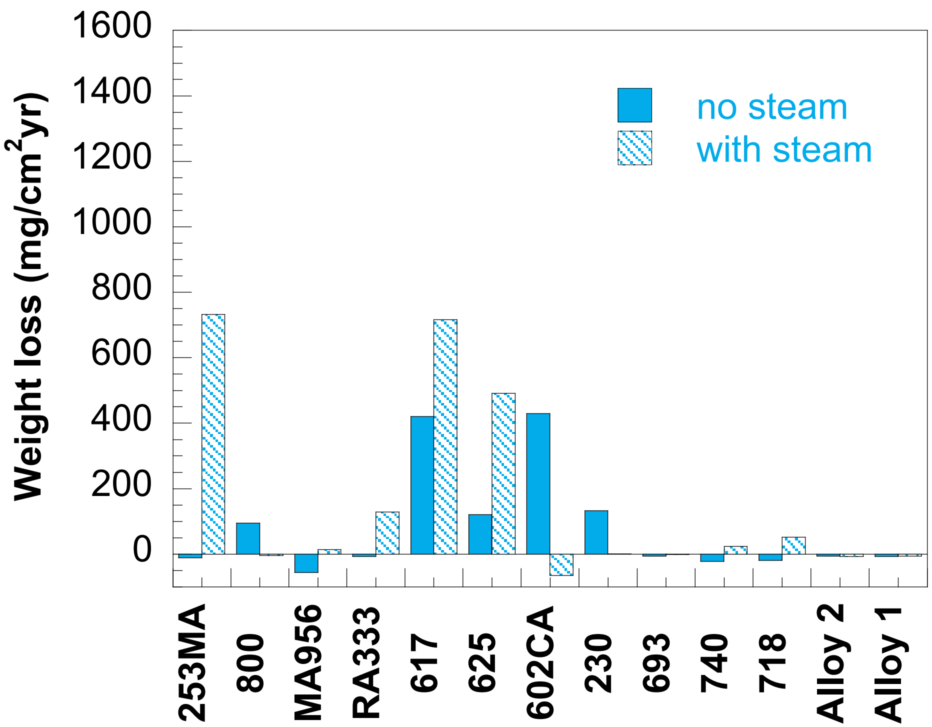
# *Weight Loss Data at 750°C to Ash and Low-$pO_2$ with Steam*

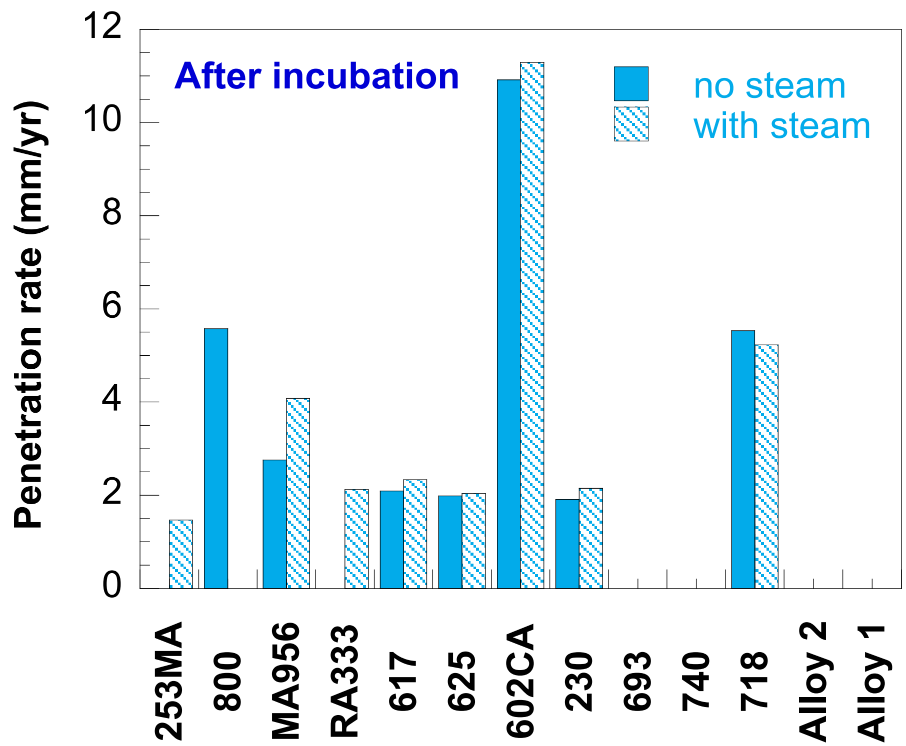


# *Incubation time*



# *Weight Loss and Penetration Data after Exposure at 750°C to Ash and Low-$pO_2$*



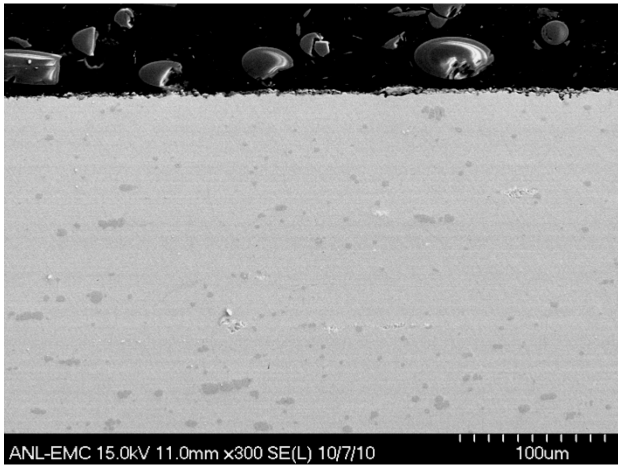
# *Alloy 230, Corrosion Tested for 1200 hr in Low $pO_2$ with Ash*

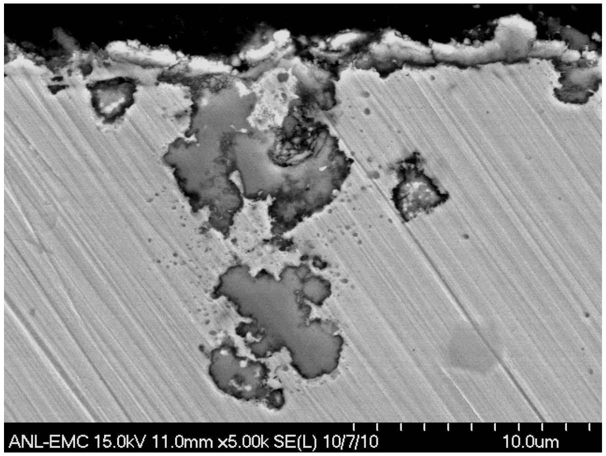
With steam
Incubation time 200h

600h 900h 1200h

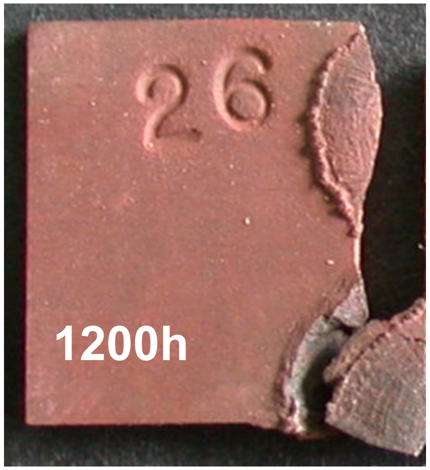
Without steam
Incubation time ~700h

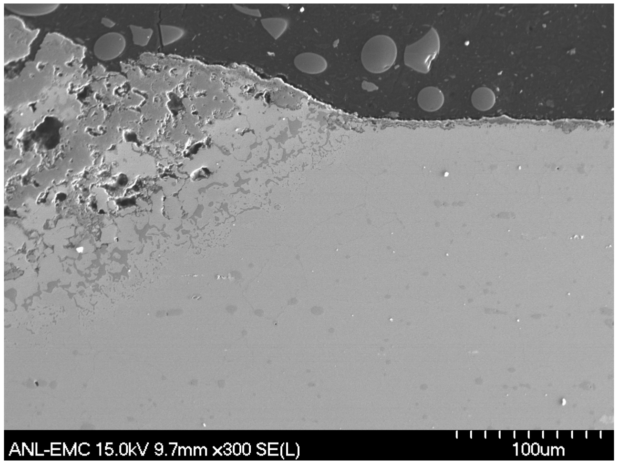
# *Alloy 602CA Before and After Incubation Time*

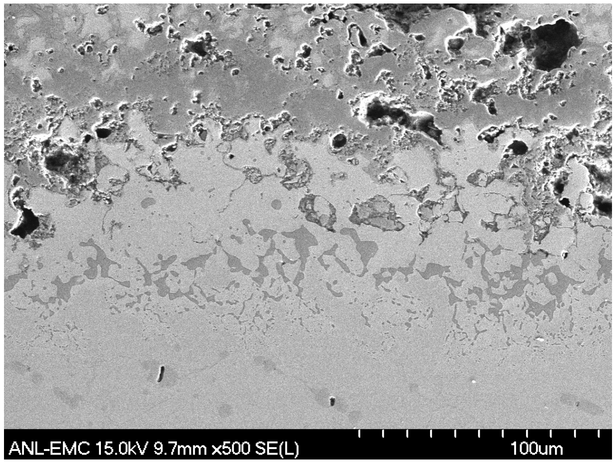




before incubation time

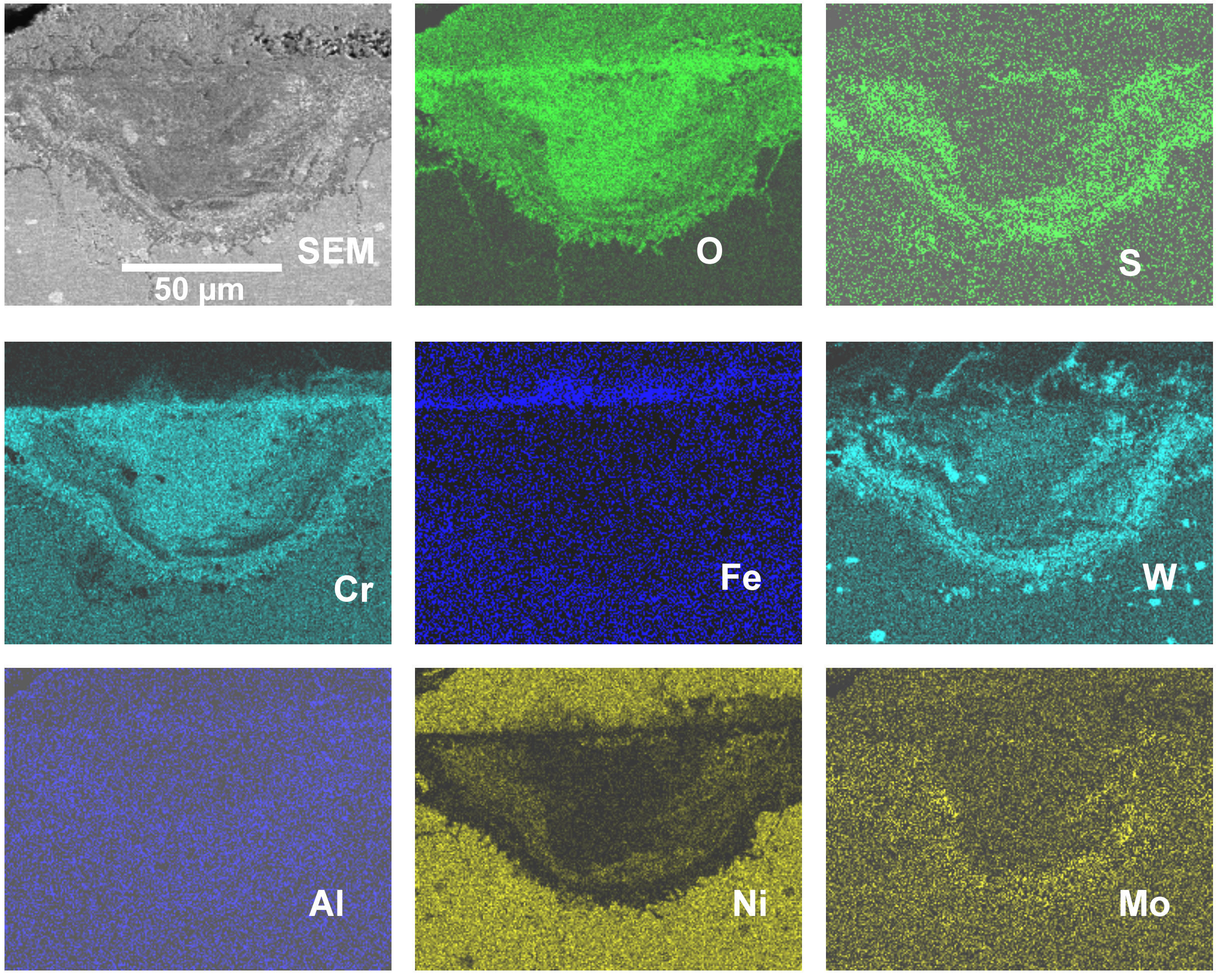


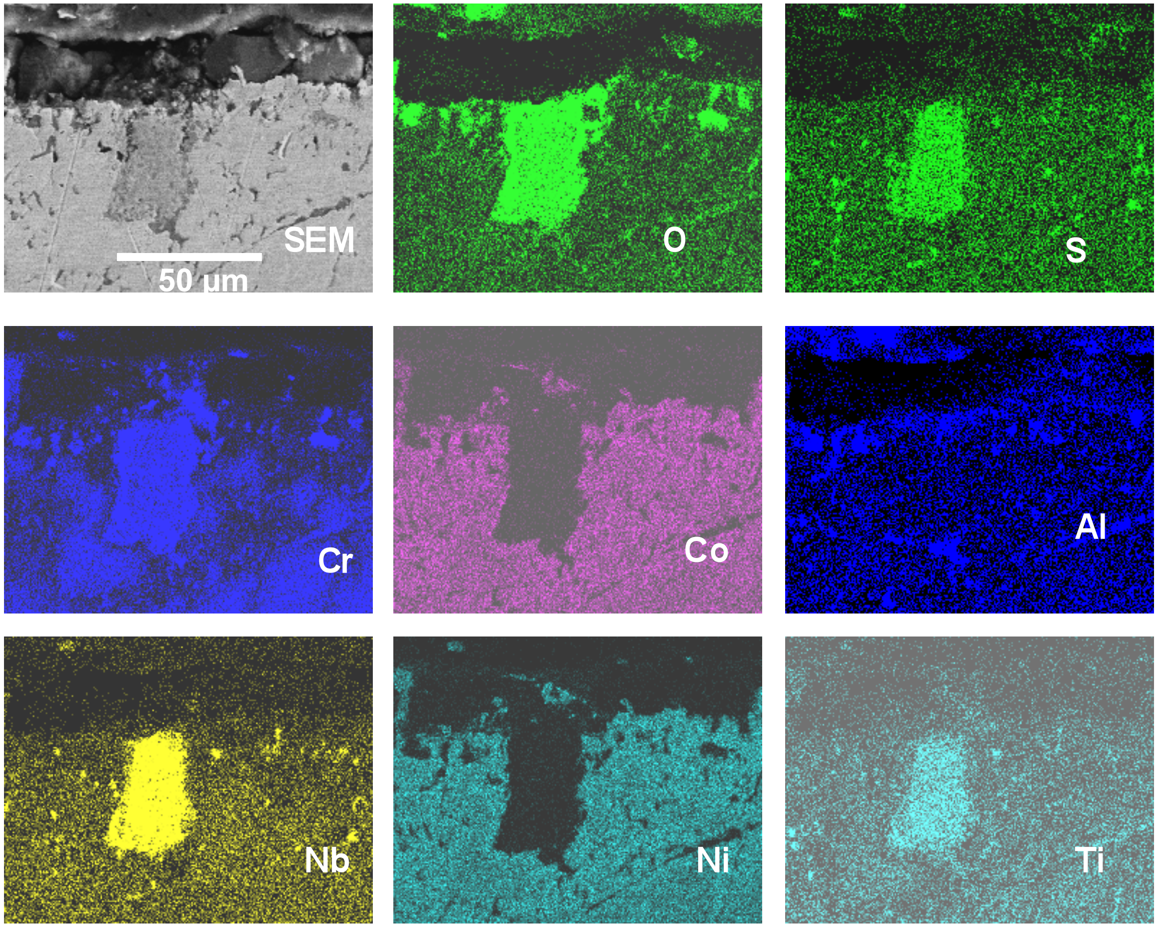

after incubation time

# *EDX Analysis of Alloy 230 Exposed to Ash*



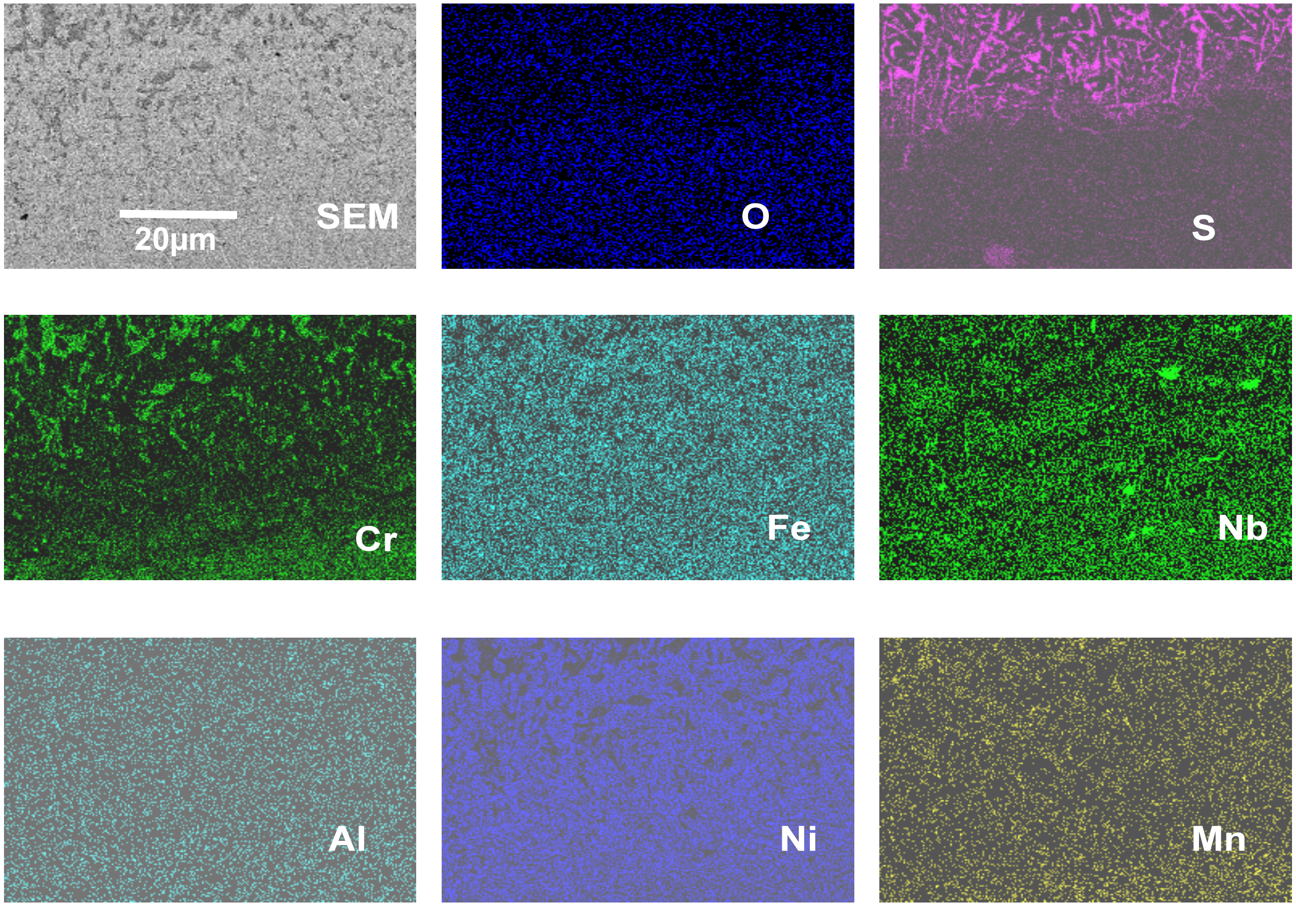

Alloy 230 **pit area**, after 600-hr exposure to ash and Gas without steam at 750ºC

# EDX Analysis of Alloy 740 Exposed to Ash




Alloy 740 after 600-h exposure to ash and Gas without steam  at 750ºC

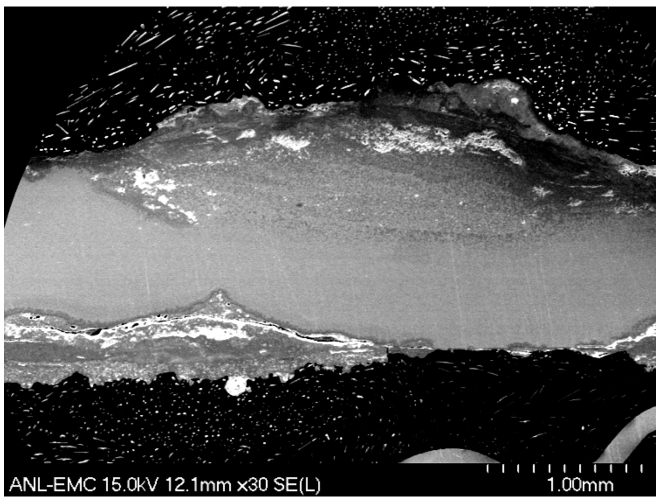
# *EDX Analysis of Alloy 718 Exposed to Ash*

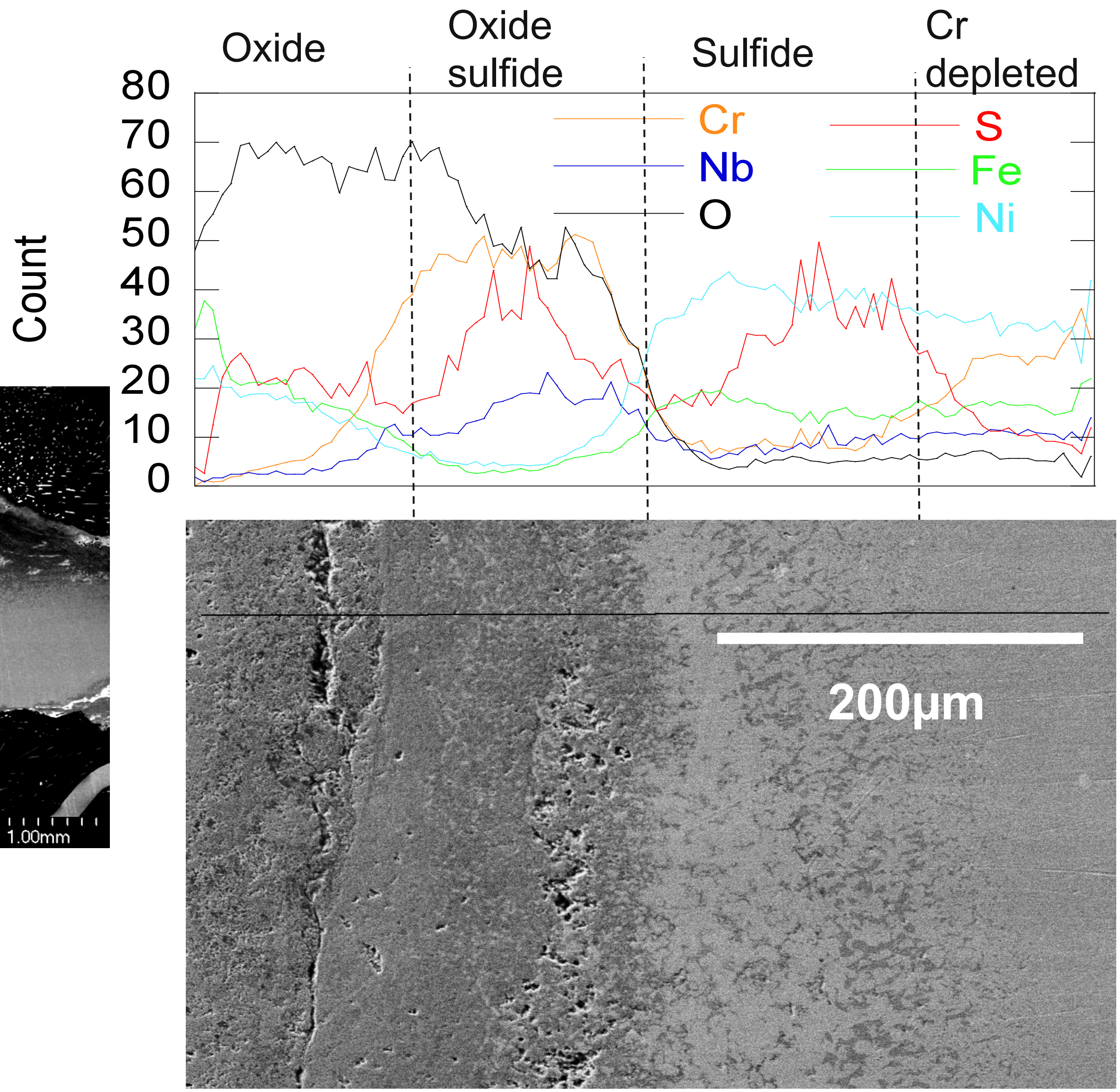



Alloy 718, after 1800-h exposure to ash and
Gas with steam  at 750ºC

# *Elemental Depth Profile of Alloy 718 Exposed to Ash*

Alloy 718



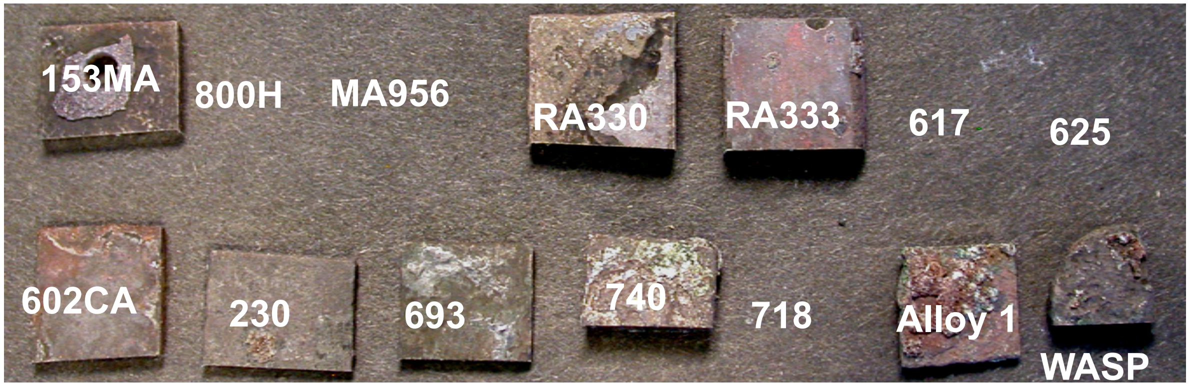



# Photograph of Specimens Exposed to Ash in High $pO_2$


600 h at 750ºC in ash and Gas with steam


600 h at 750ºC in ash and Gas without steam

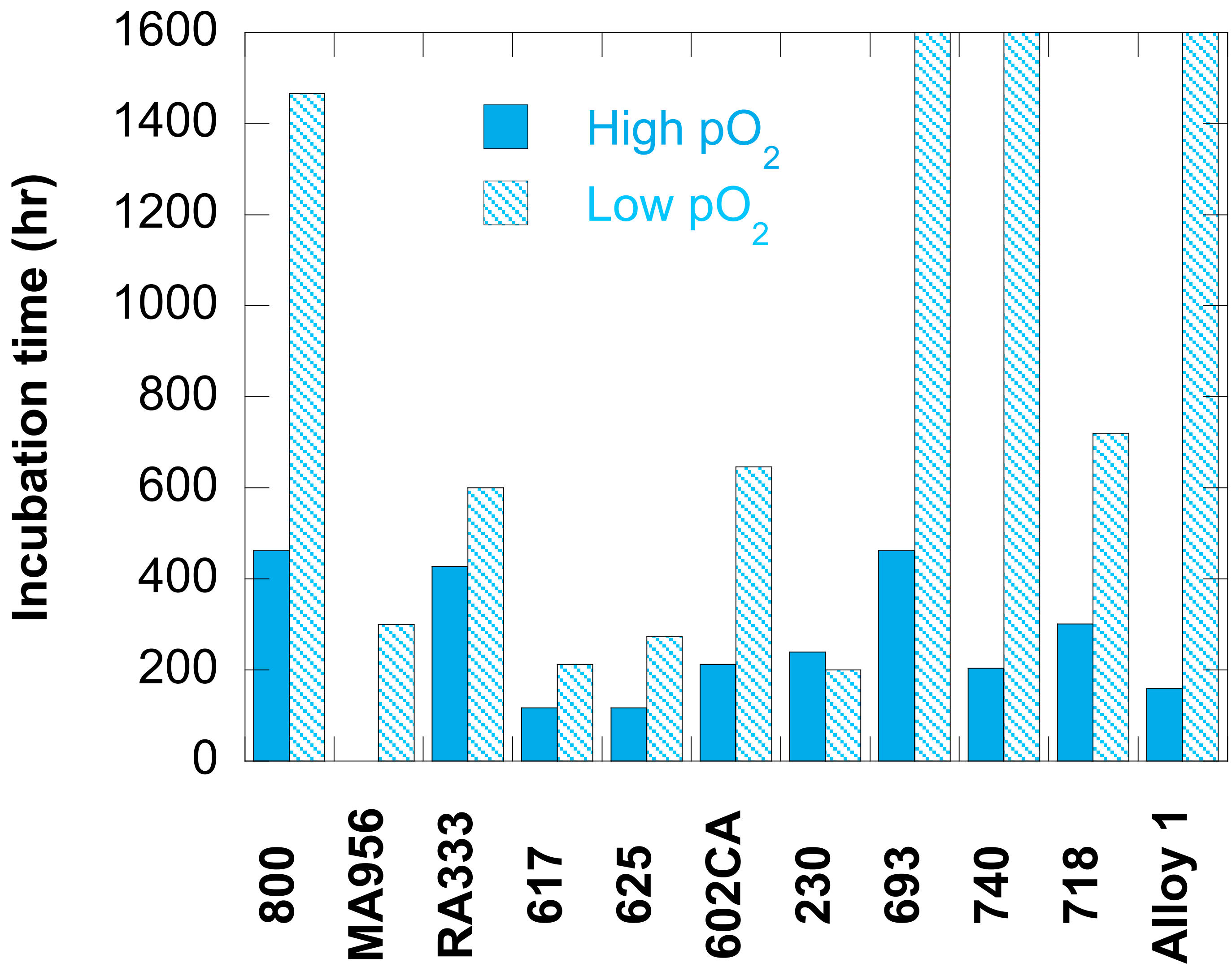
# *Photograph of Specimens Exposed to Ash in High $pO_2$*



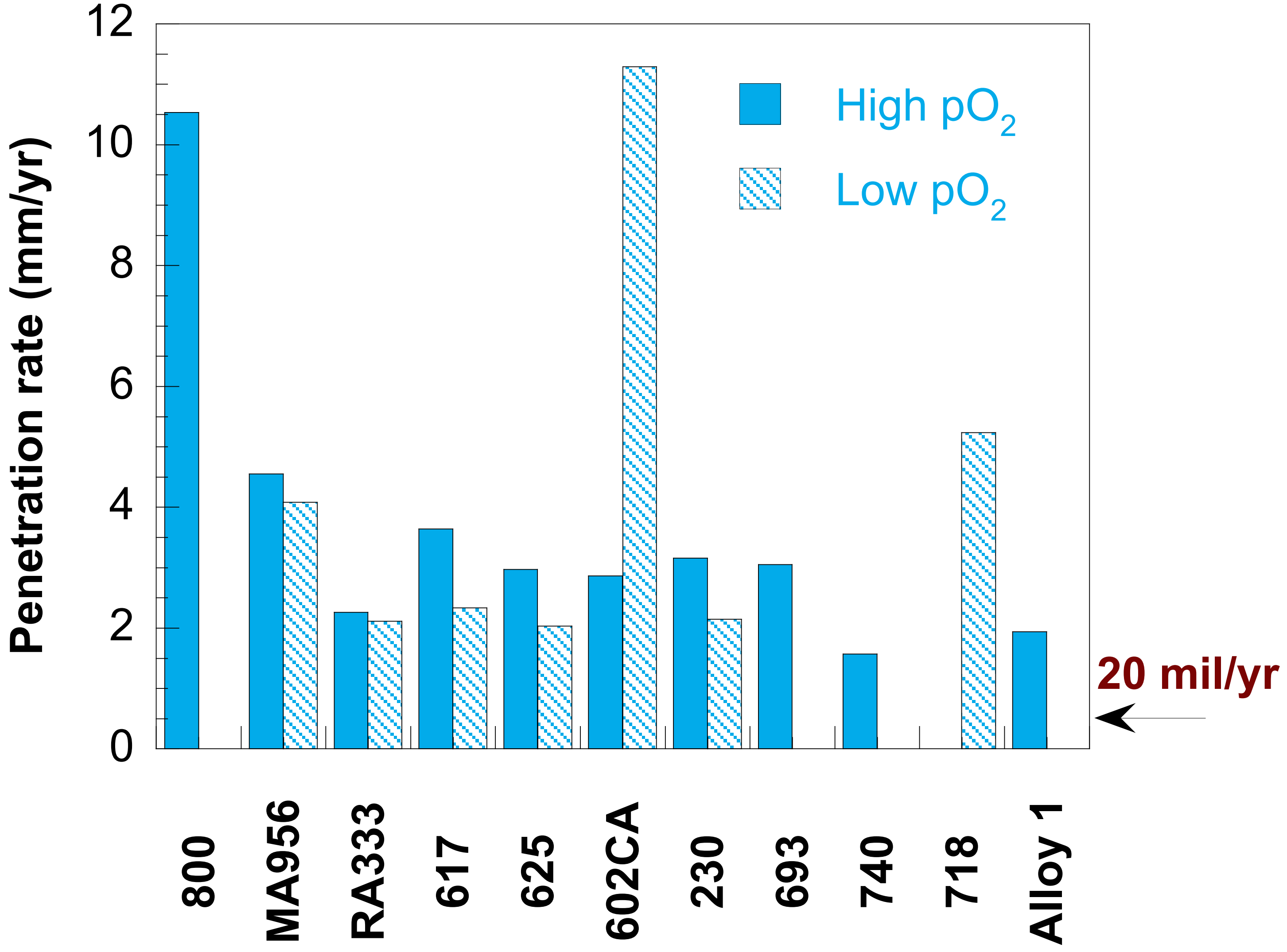

1200 hr at 750ºC in ash and Gas with steam


1200 hr at 750ºC in ash and Gas without steam

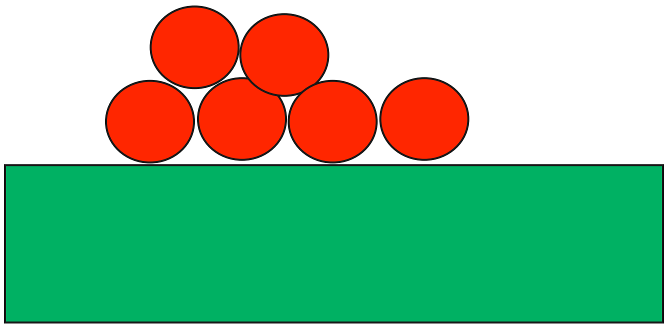
# *Effect of $pO_2$ on Incubation, Based on Ash-Exposure Tests*

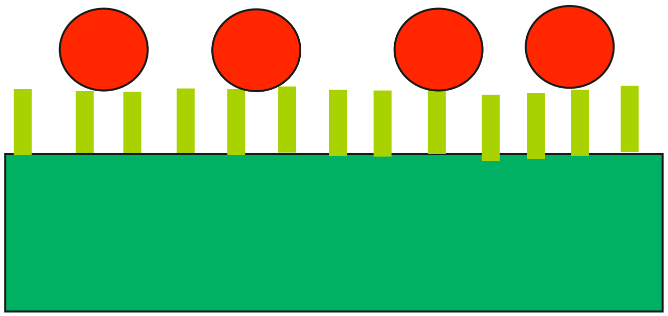


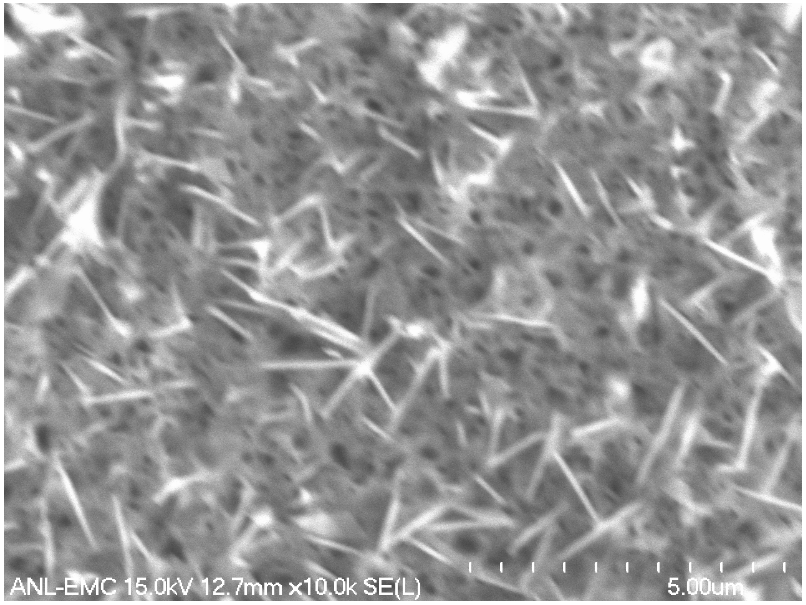
## *Penetration Data after Exposure at 750°C to Ash and in High- and Low-$pO_2$ Environments with Steam*



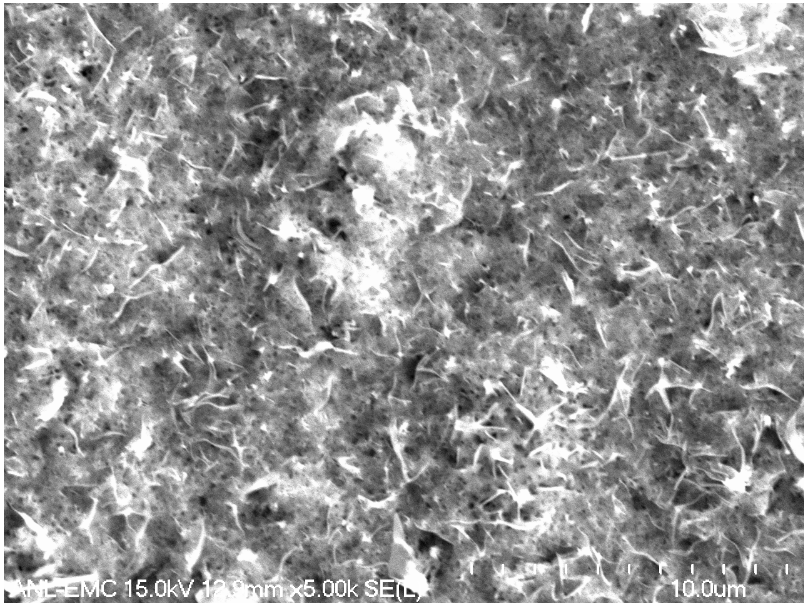
# *Nanostructured Coating Development for Corrosion Resistance*





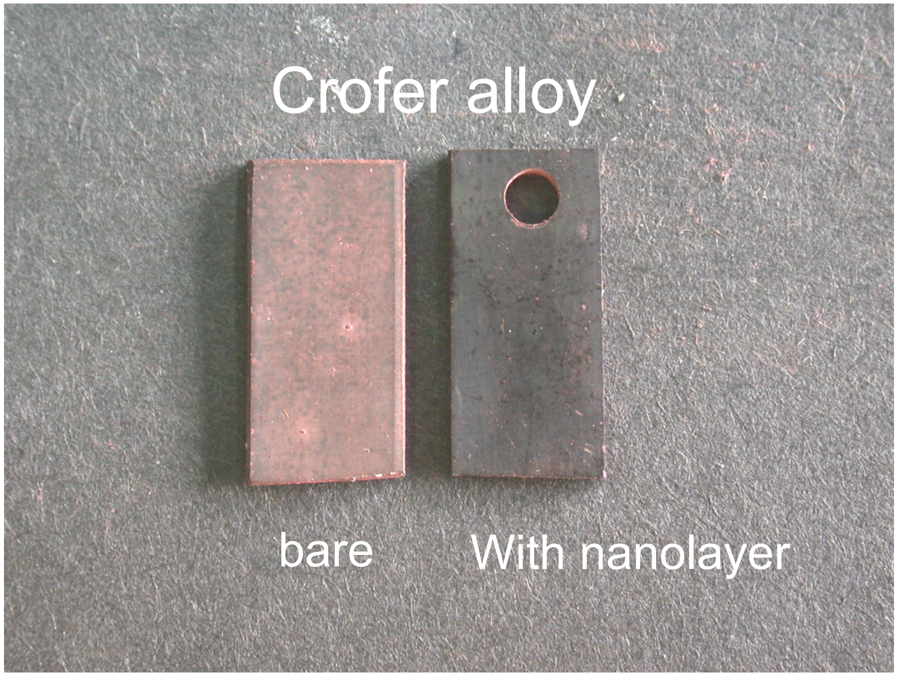



310

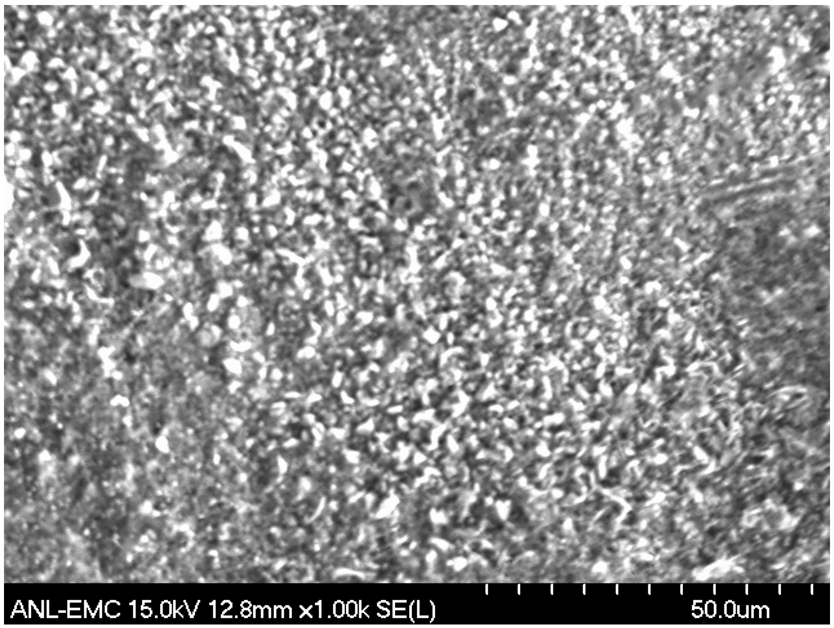



Crofer alloy

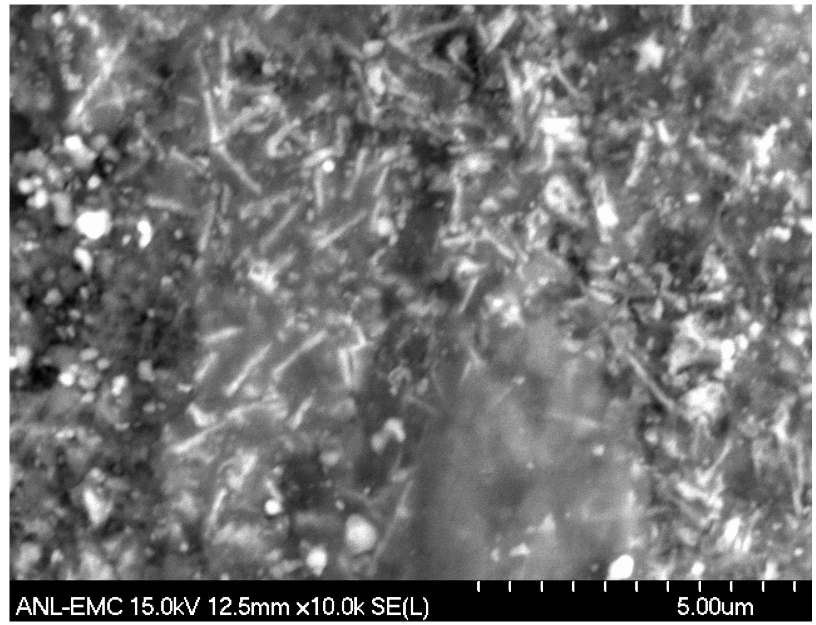
# *After exposed to Ash for 600 hr in Low-p$O_2$*

## *After Exposure to Ash for 600 hr*




Without nanolayer




With nanolayer

## *Project Summary*

- We have conducted a study to evaluate the oxidation performance of structural alloys in $CO_2$ and $CO_2$-steam environments at temperatures up to 1000°C. We believe the corrosion rates in these environments (in the absence of sulfur) are acceptable for service. However, the effect on mechanical properties is not established
- Results indicate that the oxide scales that develop on the alloys are not that protective and internal carburization of the substrate may occur
- The presence of ash (with alkali sulfates) coupled with steam in the gas environment accelerates corrosion of all structural alloys
- We have examined the role of steam and the effect of $pO_2$ on the corrosion scaling and internal penetration
- Ash/alkali sulfate effect initiates as localized corrosion in most of the alloys

## *Summary continued*

- The corrosion process generally follows parabolic kinetics in most of the alloys, when tested in gas phase environments (with or without steam) in the absence of ash
- In the presence of ash, the alloys exhibit an incubation period during which the corrosion rates are low.  Upon exceeding the incubation period, the corrosion accelerates and the process follows a linear kinetics. This is based on the microstructural examination of the tested specimens for internal oxidation/ sulfidation/penetration of the substrate alloys
- In typical oxy-fuel combustion environments used in this study, most of the alloys exhibit corrosion rates ≥ 2 mm/year, based on linear kinetics.  The rates for some of the alloys such as 693, 740, Alloys 1 and 2 could not be established due to their long incubation time
- Effort is underway to develop nanostructures surface improve the corrosion resistance of the alloys in oxy-fuel environments

## *Future Plans for the ANL research project*

- **Complete corrosion evaluation of structural alloys in oxy-fuel environments containing ash, alkali sulfates, and alkali chlorides. This includes a range of coal ash chemistry and gas environments at temperatures up to 750°C.**
- **Experimentation to mitigate corrosion of structural alloys in both advanced steam-cycle and oxy-fuel combustion systems**
  - **Conventional coatings**
  - **Ash additives**
  - **Alloy surface modification using nano-structures**